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Thermoluminescence and optically stimulated luminescence of gamma-irradiated mineral zircon

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Thermoluminescence (TL) manifested by gamma-irradiated mineral zircon has shown a strong TL peak at about 165 °C which is due to recombination of electrons and Dy^{3+} related shallow hole traps. After they have been removed by a short preheat we have observed two TL peaks at 300-320 °C and ≈420 °C, which are mainly due to recombination of electrons and Tb^{3+} related hole traps centres yielding its characteristic luminescence. The experimental results indicate that optically stimulated luminescence (OSL) is due to luminescent emission of Tb^{3+} ions and $[SiO_4]^{4-}$ groups. The deep traps related to the 420 °C TL peak contribute to the Tb^{3+} related OSL. The deep traps related to the 300-320 °C TL peak contribute to OSL associated with the luminescent emission of $[SiO_4]^{4-}$ groups.

1 Introduction The luminescence dating methods, TL and OSL might be useful to fill an important time gap in geochronometry, because often the last 500 ky, turn out to be inaccessible through other methods. The minerals used most frequently for luminescence dating are quartz and feldspars, because of their ubiquity and the ease to separate these minerals from sediments.

In the 1970's investigators have established that mineral zircon ($ZrSiO_4$) can in principle be used for TL geochronometry (see e.g. [1]). Zircon has an advantage over other minerals, which are used for luminescence dating (quartz and feldspars), because they contain radioactive U and Th impurities, which irradiate the mineral internally at dose rates much higher than those from external environmental sources. In this way the major source of variability observed in e.g. quartz-based luminescence dating, which is due to the heterogeneity of the external irradiation field, is eliminated. However it was recognized at the same time that serious problems associated with anomalous fading and the inhomogenities of zircon (due to e.g. zoning and metamictization) exist, which are responsible for intra-grain variations of the luminescence properties. Recently, these problems have been overcome by introducing a special selection procedure to obtain the most homogeneous grains of high optical quality [2]. In this way TL dating of young sediments using zircon has been successfully performed [2, 3], which leads the question whether zircon can also be used for OSL dating.

In the present paper the OSL properties of mineral zircon have been studied in relationship with TL by performing OSL measurements after repeated preheats to successively higher temperatures, i.e. pulse annealing experiments and TL after OSL bleaching measurements.

2 Experimental part The measurements have been performed on two zircon mineral samples collected from the island Ameland in the The Netherlands and from South Africa (Namaqua). Mineral

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zircon grains (75-100 µm) of high optical quality have been extracted from dune sand sediments using special procedures that include sieving, magnetic separation, and electrostatic separation/selection [2]. The experimental results are essentially the same for the two types of samples, which have been studied in this investigation.

TL and OSL measurements have been performed using a TL/OSL Risø reader; during our TL experiments we have used a 5 °C/s heating rate. For the selective detection of the TL or OSL, which are located in different spectral ranges, we have used two specially designed narrow band interferential filters with transmissions peaking at either 550 nm or 583 nm, or a broad band filter, which transmits light between 350 and 450 nm, with a transmission coefficient peaking at about 380 nm. For the OSL stimulation we have used light with a wavelength of 875 nm (IR LEDs) or red light with wavelengths longer than 700 nm from a 50 W halogen lamp together with a cut-off RG 9 Schott filter. The OSL signal stability with the temperature has been studied by performing pulsed OSL measurements, i.e by reading the OSL signal only for a very short time (few seconds) in order to avoid the optical bleaching, after subsequent thermal bleaching of the TL peaks.

The samples have been irradiated at room temperature (RT) by means of a calibrated gamma-ray source and subsequently they were preheated at about 140 °C for 0.5 h, or they were stored in the dark for several years and measured afterwards.

3 Results TL recorded on naturally irradiated zircon minerals has shown a broad peak in the 300-450 °C temperature range (Fig. 1(a) dashed curve). After gamma-irradiation at room temperature the TL curve shows additional features (Fig. 1(a) solid curve): a strong peak at about 165 °C which is due to the Dy^{3+} related shallow traps [2] and a broad TL peak in the 300-450 °C temperature range which is mainly due to deep Tb^{3+} related traps [2]. The shallow traps are related to the short-term fading effects and they have been removed by a preheat treatment at about 140 °C (Fig. 1(a), dotted curve). The treatment is equivalent with the storage in the dark for long periods of time [4].

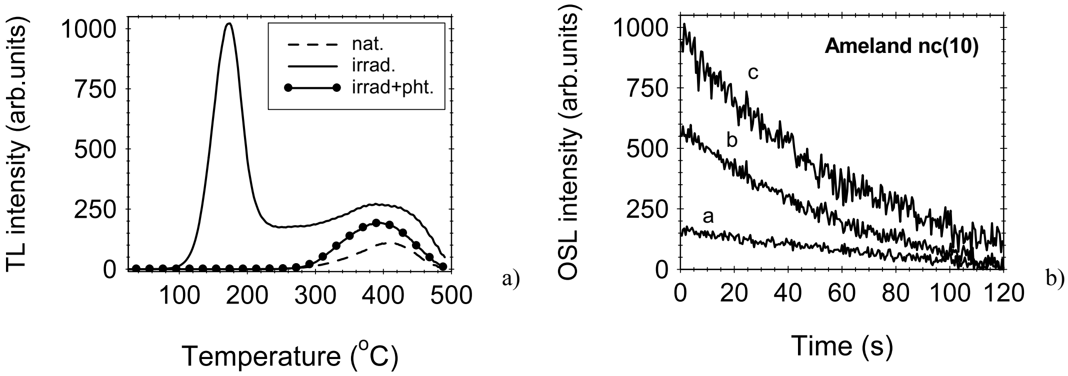

Fig. 1 (a) The TL curves recorded for mineral zircon samples (Ameland): naturally irradiated (dashed curve), laboratory irradiated with 100 Gy (solid curve) and after preheat for 0.5 h at 140 °C (dotted curve). TL was detected in the 400-700 nm range. (b) OSL decay curves using IR light stimulation (above 700 nm) of naturally irradiated mineral zircon samples recorded in the range 350-450 nm (curve a) and at wavelengths 583 nm (curve b) and 550 nm (curve c)

The OSL decay curves recorded in the 350-450 nm range and at wavelengths 550 and 583 nm using IR light stimulation (above 700 nm) are presented in the Fig. 1(b). If we use 870 nm stimulation light the OSL signal was observed only in the 350-450 nm range, while the 550nm OSL signal is absent (not shown). The TL recorded at 550 nm after optical bleaching of OSL with IR light above 700 nm (Fig. 2(a)) has shown that the two broad TL peaks from about 300-320 °C and ≈420 °C are both sensitive, the 320 °C peak drops down to ≈20% and the 400 °C peak to ≈60% (these percentages are about the same for different irradiation doses).

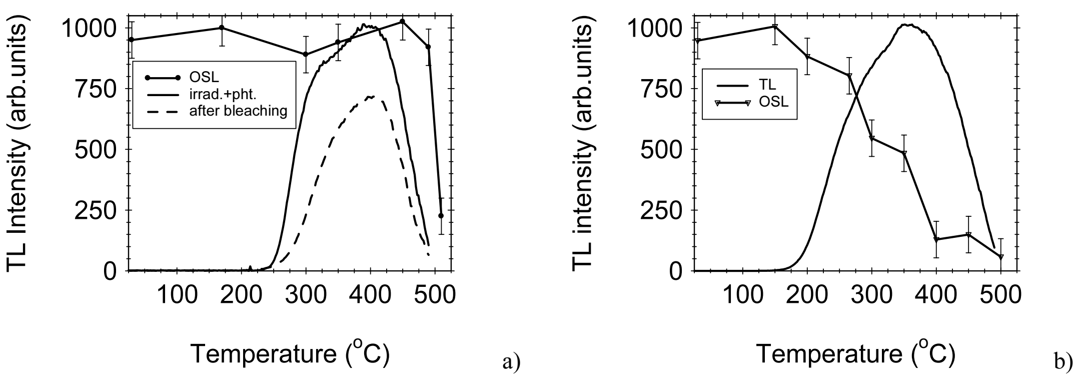

Fig. 2 (a) Pulse annealing measurements performed on mineral zircon (Ameland) using IR light stimulation (above 700 nm) and 550 nm light detection (dotted curve). The TL curves recorded at 550 nm before (solid curve) and after optical bleaching of the OSL signal (dashed curve) are also shown. The sample was gamma-irradiated at RT (100 Gy dose) and preheated at 140 °C for 0.5 h. (b) Pulse annealing measurements performed on mineral zircon (Namaqua) using 875 nm light stimulation (dotted curve). TL curve detected in the 400-700 nm range is shown for comparison. The sample was gamma-irradiated at RT (10 kGy dose) and stored in the dark for two years.

The pulse annealing experiments presented in Fig. 2(b) show that the OSL in the range 350-450 nm is thermally bleached at about 400 °C but the 550 nm OSL signal is stable up to about 500 °C.

4 Discussions In gamma-irradiated mineral zircon Dy^{3+} and Tb^{3+} impurity ions behave as hole trap centres as was shown by Electronic Paramagnetic Resonance (EPR) [5] and TL is due to their recombination with electrons released from electron traps yielding the characteristic zircon luminescence [6]. In addition, recombination of some other centres giving rise to luminescent emission of the $[SiO_4]^{4-}$ groups has been observed in the TL spectra [6, 7]. The 165°C TL peak is due to recombination of the electrons and Dy^{3+} related shallow traps and the broad TL peak in the 300-450 °C temperature range is mainly due to the recombination of electrons and Tb^{3+} related deep traps [6]. The shallow traps are responsible for the short-term fading effects and they have been removed by a preheat treatment at 140 °C. If we use 550 nm detection, which corresponds to the Tb^{3+} luminescence ($^5D_3 \rightarrow {}^7F_5$ transition [8]), the broad TL peak reveals at least two TL peaks at about 300-320 °C and ≈420 °C (Fig. 2(a)). TL curve recorded on naturally irradiated zircon minerals shows only one dominant broad peak in the temperature range 300-450 °C, which is due to the recombination with the Tb^{3+} related deep traps (Fig. 1(a)).

Previous OSL measurements performed on irradiated mineral zircon (using 514 or 633 nm stimulation) have shown that the OSL spectra consist of five bands [9]: a broad band at about 420-470 nm and a few narrow band-structures at about 480-490 nm, 570-580 nm and ≅ 550 nm; the intensities of the bands decrease during the illumination. Probably, the broad band is related to luminescent emissions of $[SiO_4]^{4-}$ groups [7]. The structured bands are probably due to a mixture of Dy^{3+} and Tb^{3+} luminescence line emissions at 482 and 578 nm for Dy^{3+} and at 489, 550, 590 nm for Tb^{3+} [8]. These measurements suggest that by IR light stimulation the electrons are released optically from the electron traps and recombine with the hole traps giving rise to the characteristic zircon luminescence. In the present case we deal with Tb^{4+} ions and centres associated with $[SiO_4]^{3-}$ groups, which act as hole traps since OSL signals have been detected at 550 nm that corresponds to the Tb^{3+} line transition $^5D_3 \rightarrow {}^7F_5$ [8] and in the range 380-390nm, which is characteristic for luminescent emission of $[SiO_4]^{3-}$ groups [7]. It is hard to believe that the OSL signal detected at 583 nm (Fig. 1(b)) is due to Dy^{3+} luminescence (i.e. $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition [8]) since the Dy^{3+} is a shallow trap that was removed by preheat (Fig. 1(a)). Most probably, the interferential filter has a weak transmission at 550 nm.

TL recorded at 550 nm after optical bleaching of OSL with IR light above 700 nm (Fig. 2(a)) has shown that the two broad TL peaks centred at about 300-320 °C and ≈420 °C are both sensitive which means that one or both these peaks are related to the OSL effect associated to the Tb^{3+} luminescence at 550 nm. The way how they are connected is shown by the pulse annealing experiments where a high stability of the OSL signal up to 500 °C was observed. This suggests that only the deep traps associated to the broad 420 °C TL peak contribute directly to the Tb^{3+} related OSL emission.

For stimulation wavelengths of 875nm OSL has been detected only in the 380-390 nm range of the $[SiO_4]^{4-}$ luminescent emission [4]. Pulse annealing experiments have shown that this OSL signal can be thermally bleached at about 400 °C (Fig. 2(b)). This suggests that the deep traps associated with the broad TL peak at about 300-320 °C (Fig. 2(a)) contribute directly to the OSL related to the luminescent emission of the $[SiO_4]^{4-}$ groups.

5 Conclusions TL shown by gamma-irradiated mineral zircon (after a preheat at 140 °C) shows two TL peaks at 300-320 °C and ≈ 420 °C which are mainly due to the recombination of the electrons released from traps and the Tb^{3+} related hole trap centres yielding the characteristic luminescence of zircon. The experimental results indicate that Tb^{3+} ions and intrinsic centres related to the $[SiO_4]^{4-}$ groups are involved as hole traps in the OSL phenomena, shown by gamma-irradiated mineral zircon (after preheat).

The deep traps related to the 420 °C TL peak contribute to the OSL associated to the Tb^{3+} luminescence at 550 nm. The deep traps related to the 300-320 °C TL peak contribute to OSL associated with the luminescent emission of $[SiO_4]^{4-}$ groups at wavelengths around 380-390 nm.

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